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The invention relates to a base paper for photographic supports, which is formed from a pulp, as well as those at least a hydrophobierendes sizing agent and at least nassfest making cationic resin contains a method to the production of the base paper.

It is known to use reciprocally with hydrophobic resin layers coated paper as carrier material for wet photographic layers which can be developed. Such a carrier material consists of a base paper also on both surfaces applied polyolefin resin coats, of which that contains the photographic layers first located coat usually at least a light reflective pigment, like TiO₂.

The polyolefin coating protects the paper laminar from the penetration of water or aqueous photographic processing liquids.

In order to prevent the penetration of these liquids at the edges of the coated paper, the base paper hard is glued. As glue means for photographic base papers are both reactive substances, e.g. Alkyl ketene dimer, and not reactive substances, e.g. higher fatty acids, known. Reactive glue means become usually neutral processed together with a cationic resin, while reactive glue means bottom addition of aluminium ions do not become acidic processed. Beyond that there is a combination of these two gluing procedures.

Those acting glue means become hydrophobierend the fiber suspension admixed and by addition of the aids on the surface of the fibers deposited. Such an aid is in the case of an acidic gluing for example an aluminium salt, in the case of the neutral gluing for example a cationic PP polyamine epichlorohydrin resin, which predominantly comes together with C16 to C18-Alkylketendimer to the use. In addition, other cationic substances like cationic polyacrylamides, kationisierte starch or polyethyleneimines are suitable in certain cases for the improvement of the retention and for the fixation from reactive sizing agents in the paper sheet.

By the attachment of the glue means at the surface of the pulp fibers the connection between the fibers is weaker in a glued paper as in a not glued paper. In order to improve the paper firmness, the pulp other aids become added. To it water-soluble resins, like polyvinyl alcohol, belong anionic polyacrylamide and various starch derivatives. In the DE-OS 32 10 621 for example the use of anionic polyacrylamide as well as cationic starch and in the DE-OS 33 28 463 becomes a combination of cationic resin with anionic strong phosphoric acid ester described.

Adverse one at an hard gluing of the base paper is not however only the firmness loss, but also by the use flock-end acting additions to adversely affected sheet forming. This is justified in the fact that by the addition by cationic substances the glue means at the fiber surface is not only retendiert, but strengthened fibrous material flakes develop, because the repulsive negative charges of the fibers become by the cationic substances to a large extent neutralized and fiber fiber archings facilitated.

The fibrous material flakes have the homogeneity and the surface finish of the base paper (formation) in dependence of the used in each case materials and of mechanical engineering apparatuses varying size and distribution in the paper sheet and to determine.

A reduction of the bath penetration at the cut edges causing the combined use of cationic and anionic water-soluble resins e.g. became. in DE-OS 32 10 621 and DE-PS 36 06 806 described.

In neutral glued papers the effected combined use of anionic and cationic resins a deterioration of the formation.

A good paper formation is in particular with photographic base papers of importance, since a connection between the fiber distribution of the Papierunterlage exists and so called "mottle" late developed photographic image.

With "mottle" become fluctuations of the optical density (density) in the photographic image referred. Intending for this phenomenon is the surface of the carrier material. Uneven surfaces lead even with absolute uniform coating application to flow features in the layer, which become more visible in the final image as "mottle". The unevenness of a paper is into strong measures of the fibrous structure of the cellulose and of the formation of cellulose flakes certain during sheet forming. That also still affects itself with coated papers.

Additional one to the mentioned above deterioration of the formation decreases/goes back the frequent structure firmness of the paper sheet, because isolated flakes from anionic and cationic resin develop, which are incorporated without solidifying effect in the paper structure.

In order to go around the flocculation problems, attempted, the pulp suspension of nonionic polymers, became e.g. Polyvinyl alcohol, starch, to admit. This leads to a certain improvement of sheet forming and the surface finish; the retention of these cloths is however significant poorer, which leads to the contamination of the sewage system and to deposits in the paper machine.

It is therefore object of the instant invention making a base paper available for photographic supports which does not have

the described disadvantages.

Beyond that it is object of the instant invention to suggest a method to the production of a base paper after which the properties specified above are improved and a better retention and thus clean a cycle guidance can become achieved.

♣ 100

The object becomes dissolved by the fact that the base paper from a pulp is formed, which nassfest additional to at least a hydrophobierenden sizing agent and at least one making resin alkyl ammonium groups an exhibiting starch or alkyl ammonium groups and phosphate groups an exhibiting starch contains.

As suitable hydrophobierende sizing agents prove both reactive sizing agents and dimerisierte alkyl ketenes, epoxidized fatty acid amides or fatty acid anhydrides and non reactive sizing agents like higher fatty acids and salts of higher fatty acids. A particularly preferred dimerisiertes alkyl ketene exists to at least 50% of Behenylketen or another alkyl ketene with more than 18 C-atoms in the alkyl radical. In addition, two or more hydrophobierende sizing agents can be contained in the paper. Reactive with non reactive sizing agents combined can become.

A cationic resin is each resin with cationic groups, conventional in the papermaking as wet strength agents. They serve usually for the wet solidification and for the Retendierung of reactive sizing agents. They can become however both in combination with reactive and with non reactive sizing agents used. In a preferable embodiment the cationic resin is a polyamine or a PP amine resin modified with epichlorohydrin. Other suitable resins e.g. are. Urea/formaldehyde resins, Melamin/Formaldehydharze, polyethyleneimines and Polyethyleniminderivate.

The starch contained as an other component in the pulp is alkyl ammonium groups or alkyl ammonium and phosphate groups an exhibiting starch.

Suitable in particular is an amphoteric or cationic corn or potato starch. That content at ammonium groups in the starch according to invention amounts to 0.9 to 2.5 mol. %. That content at phosphate groups can to 0.3 mol. % amount to.

The amount of the used starch according to invention in the pulp amounts to preferably 0.5 to 2.0 Gew.%, related to pulp (atro). Particularly preferred becomes however an amount from 1 to 1.5 Gew.%,.

As anionic inorganic particles are suitable in particular a colloidal silica, a colloidal aluminum-modified silicic acid or a colloidal aluminum-modified silicate.

The amount anionic inorganic particles in the pulp preferably amounts to to 0.2 Gew.%, related to the dry pulp fibers. In one particularly preferable embodiment of the invention become anionic inorganic particles in an amount of 0,02 to 0.1 Gew.%, used.

The base papers according to invention become in known manner prepared with the help of a paper machine. The Papierfaserstoffpulle beside pulp fibers can contain still synthetic fibers, inorganic or organic fillers, white pigment, dye or color pigment, optical brightener, Antioxidantien and/or other with the production additives of photographic conventional paper supports.

In the frame of the invention process the various components in different order and at the various paper manufacturer can become known sites of the pulp suspension added.

Regarding the achievement of optimum results the starch according to invention in the sequence before the anionic inorganic particles becomes into the fibrous material suspension admixed with a preferable embodiment of the invention. Anionic inorganic particles become the preferred so called thin material before the headbox supplied.

Furthermore the paper can be surface-glued, e.g. with polyvinyl alcohol, starch, gelatin among other things, and becomes reciprocal after completion and smoothing in conventional manner with synthetic resin coated.

The synthetic resin coat can as extrusion coating from the melt, when dispersion coat, when coat ray hardness that mixtures take place or on other known manner. The paper coated with resin serves, if necessary also after application other layers and after application of an adhesion-improving pretreatment, as carrier for arbitrary photographic layers.

The invention becomes more near explained in the subsequent examples.

Example 1

A mixture from 100 Gew.%, hardwood sulfate cellulose became milled with a Stoffdichte of 4% up to a freeness of 35 DEG SR. The pulp suspension became then sizing agents, starch according to invention and other auxiliaries corresponding table 1 added and from it approx. 170 g/m< 2> heavy base paper made. The paper was surface-glued in known manner with an aqueous solution, which contains 3.33 Gew.%, polyvinyl alcohol and 3.33 Gew.%, CaCl₂, and smoothed.

<tb>< TABLE> Id= Tabelle 1 Columns= 7

<tb>

<tb> Head Col 1: Leimstoffe*

<tb> Head Col 2 tons of 7: Sample

<tb>

<tb> SubHead Col 1:

<tb> SubHead Col 2:

1a

<tb> SubHead Col 3: 1b

<tb> SubHead Col 4: 1K

<tb> SubHead Col 5: 1d

<tb> SubHead Col 6: 1e

<tb> SubHead Col 7: 1f

<tb>

<tb> SubHead Col 8: Corn starch with alkyl ammonium groups

<tb> 0.9 Mol.%,< September> -< September> -< September> -< September> 1.5< September> -

<tb> 1.7 Mol,%< September> 0.5< September> 1.0< September> 1.2< September> 2.0< September> -< September> -
 <tb> 2.5 Mol,%< September> -< September> -< September> -< September> -< September> -< September> 1,5
 <tb> polyamide/polyamine Epichchlorhydrin resin< September> 0.7< September> 0.7< September> 0.7< September>
 0.7< September> 0.7< September> 0,7
 <tb> alkyl ketene dimer< September> 0.5< September> 0.5< September> 0.5< September> 0.5< September> 0.5< September> 0,5
 <tb> Epoxyd.Fettsäureamid< September> 0.05< September> 0.05< September> 0.05< September> 0.05< September> 0.05< September>
 0.05< September> 0,05
 <tb> white toners< September> 0.05< September> 0.05< September> 0.05< September> 0.05< September> 0.05< September> 0.05< September> 0,05
 * All quantity specifications in this table are Gew,%, related to the pulp

<tb>< /TABLE>

Example 2

Analogous example 1 170 g/m 2< became> heavy base papers with the analyzed subsequent prepared in table 2 listed cloths and.

<tb>< TABLE> Id= Tabelle 2 Columns= 4

<tb>

<tb> Head Col 1: Glue materials

*

<tb> Head Col 2 tons of 4: Sample

<tb>

<tb> SubHead Col 1:

<tb> SubHead Col 2: 2a

<tb> SubHead Col 3: 2b

<tb> SubHead Col 4: 2C

<tb> potato starch with 1,7 Mol,% ammonium groups and 0.2 Mol,% phosphate groups< September> 1.50< September> 1.50< September> 1,50

<tb> PP/polyamine epichlorohydrin resin< September> 0.40< September> 0.40< September> 0,40

<tb> alkyl ketene dimer< September> 0.50< September> 0.50< September> 0,50

<tb> Epoxyd. Fatty acid amide< September> 0.05< September> 0.05< September> 0,05

<tb> anion. Silicate< September> 0.05< September> 0.10< September> 0,20

<tb> white toners< September> 0.05< September> 0.05< September> 0,05

* Quantity specifications in Gew,%, related to the pulp

<tb>< /TABLE>

Example 3

A pulp suspension from 50 Gew,% hardwood sulfate cellulose and 50 Gew,% hardwood sulfite cellulose sizing agents and starch according to invention became corresponding table 3 added and from it approx. 190 g/m 2< became> heavy base papers made.

<tb>< TABLE> Id= Tabelle 3 Columns= 4

<tb>

<tb> Head Col 1: Glue materials

*

<tb> Head Col 2 tons of 4: Sample

<tb>

<tb> SubHead Col 1:

<tb> SubHead Col 2: 3a

<tb> SubHead Col 3: 3b

<tb> SubHead Col 4: 3c

<tb> corn starch with 1,7 Mol,% alkyl ammonium groups< September> 0.9< September> 0.6< September> 0,3

<tb> PP/polyamine epichlorohydrin resin< September> 1.2< September> 1.2< September> 1,2

<tb> alkyl ketene dimer< September> 0.5< September> 0.5< September> 0,5

<tb> Epoxyd. Fatty acid amide< September> 0.05< September> 0.05< September> 0,05

<tb> white toners< September> 0.05< September> 0.05< September> 0,05

* Quantity specifications in Gew,%, related to the pulp

<tb>< /TABLE>

Comparison example V1

A pulp suspension from 100 Gew,% hardwood sulfate cellulose the subsequent cloths added became:

<tb>< TABLE> Columns= 2

<tb> anionic starch (Emcoat KPS)< September> 1.50 Gew,%

<tb> alkyl ketene dimer< September> 0.50 Gew,%

<tb> polyamide/polyamine epichlorohydrin resin< September> 0.70 Gew,%

<tb> Epoxyd. Fatty acid amide< September> 0.05 Gew,%

<tb> white toners< September> 0.05 Gew,%

<tb>< /TABLE> From this 170 g/m 2< became> heavy base paper made.

Comparison example V2

A pulp suspension from 50 Gew,% hardwood sulfite cellulose and 50 Gew,% hardwood sulfate cellulose the subsequent cloths added became:

<tb>< TABLE> Columns=2

<tb> polyacrylamide< September> 0.3 Gew,%

<tb> alkyl ketene dimer< September> 0.5 Gew,%

<tb> polyamide/polyamine epichlorohydrin resin< September> 1.2 Gew,%

<tb> Epoxyd. Fatty acid amide< September> 0.05 Gew,%

<tb> white toners< September> 0.05 Gew,%

<tb>< /TABLE> From this 190 g/m 2< became> heavy base paper made.

Examination of the base papers prepared in accordance with the examples and comparison examples

A part uncoated were left by the made paper samples and tested, another part were submitted in each case reciprocally in known manner with polyethylene coated and in this form of an examination. For the evaluation the subsequent test methods were consulted:

Inner strength (structure firmness)

The structure firmness became certain after TAPPI RC 308 with a Scott bond interlaminar strength examiner (Internal bond Impact tester Model B). The number data in the subsequent tables are in each case averages from 5 individual measurings. The measurement values become in 1/1000 foot x pound (ft.lb/1000) indicated.

Edge-penetrate from developer (KE)

The paper samples coated with polyethylene became in required sample-large for 14 minutes in a commercial Color Entwicklerbad (T = 30 DEG C) immersed. After intermediate splash-down, treatment with commercial fixing solution and final splash-down became the patterns dried and with a measuring magnifying glass the depth of penetration (mm) of the developer solution at the cut edge measured. The zone of the developer penetration is to be recognized as brownishly discoloured edge strip.

Stiffness

The rigidity values of the Rohpapiere became 29,69 determined with the flexural rigidity examiner of Lorentzen & Wettre, in accordance with norm SCAN-P. The measurement values become in mN indicated.

Formation

The formation becomes in an internal examined on the basis datum locators by a note scale from 1 to 5 judged, whereby the note 1 for a very uniform and the note 5 stand for much a "cloudy" appearance of the paper structure in the transmitted light.

Retention

The retention (entire retention, %) became after from the company PAPER Research of material, Inc. developed "Britt" dynamics drainage year method (DDJ - method) determined.

Furthermore routine ones became also different properties of the base paper such as surface number, tensile strength, adhesion of the polyethylene layers and photo-chemical properties tested. The results move however in the known frame and for the evaluation of the Erfindung were not consulted.

The test results are in table 4 assembled. For the evaluation of the invention the entirety of the tested properties should be consulted.

As from table 4 apparent is successfully while maintaining the required strength and stiffness a substantial improvement of the formation and thus surface finish to reach (S. See. V1 and Bspl. 1-3).

Also an increase of the entire retention and thus a cleaner cycle guidance can become with the gluing according to invention achieved.

EMI15.1